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"Improved process for pre-treatment of stainless steel mandrels used in electroforming of copper foils".

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Hafi Marg, New Delhi, India, an Indian registered body incorporated under the Registration of Societies Act (Act XXI of 1860).

The following specification describes the nature of this invention.

PRICE: TWO RUPEES

150472

This is an invention by Balkunje Anantha Shenoi, Scientist, Sandip Kumar Roy, Scientist, Venkataraman Sivan, Scientist, Subbiah John, Senior Technical Assistant and Mandagopal Varadappa Shanmugam, Junior Scientific Assistant, all employed in Central Electrochemical Research Institute, Karaikudi - 623006, all Indian nationals.

This invention relates to the development of a pretreating step for stainless steel used in electroforming of copper foils.

The drawbacks of this mandrel so far used lie in the fact that they fail to give (a) pore free foil (b) shining mandrel surface and (c) reproducibility of obtaining copper foils of similar characteristics.

Though a pretreated titanium mandrel overcomes the above difficulties, however, it has the following manor defects.

(a) Time of pretreatment for titanium mandrel is very critical. Prolonged treatment attacks titanium producing a dull black layer over titanium which leads to wrinkles in the formed copper foil.

(b) Titanium is costlier than stainless steel.

The object of the present invention is to obviate the above difficulties encountered in electroforming of copper foils with a treated titanium mandrel by using a stainless steel mandrel after a suitable chemical treatment of the surface.

To this end, the invention broadly consists in applying a chemical treatment (2-10 minutes) to a polished stainless steel mandrels with one of the following solutions :

1.	Cupric chloride	10 - 25 g/l
	Hydrochloric acid (Sp. gr. 1.18)	250 - 500 ml/l
	Methanol	10 - 50 ml/l
2.	Hydrochloric acid(Sp. gr. 1.18)	25 - 50 ml/l
	Chromic acid	10 - 50 g/l
3.	Potassium ferricyanide	20 - 100 g/l
	Sodium hydroxide	5 - 30 g/l

The copper foils obtained after such treatments were possessing a shining surface, smooth and pore free.

The following is the flow chart for this process.

Stainless sheet
↓
Polishing and buffing
↓
Degreasing
↓
Electrocleaning
↓
Washing
↓
Chemical treatment
↓
Washing
↓
Electroforming from acid copper sulphate bath

The following are the examples to illustrate this process and not to limit the scope of this invention.

EXAMPLE 1

304 stainless steel mandrel of size 300 mm x 300 mm x 3 mm(thick) was polished and buffed in usual manner till a scratch free surface was obtained. The mandrel was then degreased with trichloroethylene and electrocleaned in alkaline solution. The stainless steel mandrel was treated with a solution containing 10 g/l of cupric chloride, 250 ml/l of hydrochloric acid and methanol 15 ml/l for 5 minutes at room temperature. The mandrel was thoroughly washed with distilled water. Electroforming of copper was then carried out from an acid copper sulphate bath for a predetermined time. The foil was then peeled off, washed and dried. It was smooth, lustrous, pore free and wrinkles free.

EXAMPLE 2

316 stainless steel mandrel of size 600 mm x 600 mm x 6 mm after usual polishing, buffing, degreasing, electrocleaning, washing cycle, chemical treatment was carried with a solution containing cupric chloride 25 g/l hydrochloric acid 500 ml/l and methanol 50 ml/l for 2 minutes. The treated mandrel was thoroughly washed, rinsed with distilled water, and electroforming was carried out from an acid copper sulphate bath for a predetermined time. The foil was then detached from this mandrel, washed and then dried. The mandrel facing side of the foil was found to be smooth, shining, free from pores and wrinkles.

EXAMPLE 3

302 stainless steel sheet of size 300 mm x 300 mm x 6 mm after

polishing, buffing, electrocleaning, washing and cleaning as indicated in the above examples was treated with a solution of hydrochloric acid 25 ml/l (sp. gr. 1.18) and chromic acid 10 g/l for 5 minutes at room temperature. The mandrel was then thoroughly washed with distilled water and electroforming was carried out from an acid copper sulphate bath for a predetermined time. The foil was then removed from the mandrel, washed thoroughly and dried. The mandrel facing surface of the foil was found to be lustrous, smooth, free from pores and wrinkles.

EXAMPLE 4

304 stainless steel sheets of size 600 mm x 600 mm x 3 mm were polished and buffed, degreased and electrocleaned as indicated above. The mandrel was then treated with hydrochloric acid (sp.gr. 1.18) 50 ml/l and chromic acid 25 g/l for 2 minutes at room temperature. The mandrel was then washed thoroughly with distilled water and transferred to an acid copper sulphate bath and electroformed for a predetermined time. The foil was then removed from this mandrel, washed thoroughly and dried. The mandrel facing surface was found to be lustrous, smooth, free from pores and wrinkles.

EXAMPLE 5

316 stainless steel sheets of size 300 mm x 300 mm x 3 mm were pre-cleaned as before. The sheet was then treated with potassium ferricyanide 20 g/l and sodium hydroxide 5 g/l for 10 minutes. The mandrel was then thoroughly washed with distilled water and transferred to an acid copper sulphate electroforming bath. Electroforming was carried out for a predetermined time. The foil was then removed from the mandrel, washed thoroughly and dried. The mandrel facing side of the foil was found to be lustrous, smooth and free from wrinkles and pores.

EXAMPLE 6

302 stainless steel mandrels of size 600 mm x 600 mm x 6 mm were pre-cleaned as before. The mandrel was then treated with a solution containing potassium ferricyanide 100 g/l and sodium hydroxide 30 g/l for 2 minutes. The mandrel was washed thoroughly with distilled water. Electroforming was carried out for a known time from an acid copper sulphate bath. The foil was then removed from the mandrel, washed and dried. The mandrel facing side of the foil was found to be lustrous, smooth, pores and wrinkles free.

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The following are the main advantages of this invention :

1. The electroformed copper foils are pore free.
2. The side facing the mandrel is found to be lustrous, smooth and shining.
3. The peeling off of the foil is made easy.
4. Time of pretreatment is not critical.
5. Stainless steel is cheaper than titanium.
6. Reproducibility of obtaining copper foils of similar surface finish.
7. The foils obtained are free from wrinkles.
8. The chemicals used are indigenously available and are cheap.

Dated this 20th day of December 1978

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THE PATENTS ACT. 1970

COMPLETE SPECIFICATION

(Section—10)

"Improved process for pre-treatment of stainless steel mandrels used in electroforming of copper foils".

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Rafi Marg, New Delhi, India, an Indian registered body incorporated under the Registration of Societies Act (Act XXI of 1860).

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

This is an invention by Balkunje Anantha Shenoi, Scientist, Sandip Kumar Roy, Scientist, Venkateraman Sivan, Scientist, Subbiah John, Senior Technical Assistant, Nandagopal Varadappa Shanmugam, Junior Scientific Assistant, all of them employed in the Central Electrochemical Research Institute, Karaikudi 623006, all Indian nationals.

This invention relates to an improved process for pre-treatment of stainless steel mandrels used in the electroforming of copper foils.

Hitherto it has been proposed to treat stainless steel mandrels

i) in an aqueous solution containing dichromate and/or chromic acid to form a passive oxide film on the mandrel surface or

ii) in an aqueous solution containing nitric acid.

The main drawbacks of the hitherto known processes are that mandrels treated in the above solutions often produce a non-shiny mandrel surface and this results in the production of highly porous foils. The possibility of obtaining copper foil of similar characteristics using the thus pretreated mandrel is made difficult.

The main object of the present invention is to obviate the above difficulties encountered in electroforming of copper foils by using a suitable chemical pretreating process to obtain a treated surface to enable the production of pore free copper foils with a shiny surface on its mandrel facing side by the electroforming technique.

The main finding underlying the present invention consists in treating the stainless steel mandrel in an aqueous acidic or alkaline oxidising solution based on hydrochloric acid or sodium hydroxide containing as an oxidising agent cupric chloride, chromic acid or potassium ferricyanide at room temperature for a period of 1-15 minutes to produce a smooth and shiny mandrel for producing pore free copper foils.

The invention accordingly provides an improved process for the pre-treatment of stainless steel mandrels used in electroforming of copper foils comprising polishing, buffing, degreasing and electrocleaning the mandrel surface and then treating the same with an aqueous acidic or alkaline oxidising solution containing as an oxidising agent cupric chloride, chromic acid or potassium ferricyanide at room temperature to obtain a mandrel with a shiny surface.

The new result flowing from the process of the invention is that stainless steel mandrels pre-treated in the above solutions produce pore free copper foils with a shiny surface on the mandrel facing side.

The present invention consists of a process for pre-treating of stainless steel mandrels suitable for electroforming of copper foils which consists in polishing, degreasing, electrocleaning, chemical pre-treating, electroforming of copper foils from acid copper electrolytes and finally separating the foil from the mandrel wherein the said stainless steel mandrel is pretreated with an aqueous acidic or alkaline oxidising solution based on hydrochloric acid 250-500 ml/l or sodium hydroxide 5-30 g/l containing as an oxidising agent cupric chloride, chromic acid or potassium ferricyanide in amounts of 10-100 g/l at room temperature for a period of 1-15 minutes whereby the said pretreatment produce a treated mandrel surface for producing copper foils free from pores and wrinkles and with a shiny surface on the mandrel facing side.

The following is the flow chart of this process :

Stainless steel mandrel

↓

Polishing and buffing

↓

Degreasing

↓

Electrocleaning

↓

Chemical pretreatment in acid/alkaline oxidising solution

↓

Electroforming in acid copper electrolytes

↓

Separating copper foil from mandrel

The following are some of the advantages of this invention :

1. The electroformed copper foils are pore free.
2. The side facing the mandrel is found to be lustrous, smooth and shining.
3. The peeling off of the foil is made easy.
4. Time of pretreatment is not critical.
5. Re-producibility of obtaining copper foils of similar surface finish.
6. The foils obtained are free from wrinkles.
7. The chemicals used are indigenously available and are cheap.

The following typical examples are given to illustrate how the invention is carried out in actual practice but not to limit the scope of this invention.

Example 1

304 stainless steel mandrel of size 300 mm x 300 mm x 3 mm (thick) was polished and buffed in usual manner till a scratch-free surface was obtained. The mandrel was then degreased with trichloroethylene and electrocleaned in alkaline solution. The stainless steel mandrel was treated with a solution containing 250 ml/l hydrochloric acid and 10 g/l cupric chloride for 5 minutes at room temperature. The mandrel was thoroughly washed with distilled water. Electroforming of copper was then carried out from an acid copper sulphate bath for a predetermined time. The foil was then peeled off, washed and dried. It was smooth, lustrous, pore free and wrinkles free.

Example 2

316 stainless steel mandrel of size 600 mm x 600 mm x 6 mm after usual polishing, buffing, degreasing, electrocleaning, washing cycle, chemical treatment was carried with a solution containing 500 ml/l hydrochloric acid and 25 g/l cupric chloride for 2 minutes. The treated mandrel was thoroughly washed, rinsed with distilled water and electroforming was carried out from an acid copper sulphate bath for a predetermined time. The foil was then detached from this mandrel, washed and then dried. The mandrel facing side of the foil was found to be smooth, shining free from pores and wrinkles.

Example 3

302 stainless steel sheets of size 300 mm x 300 mm x 6 mm after polishing, buffing, electrocleaning, washing and cleaning as indicated in the above examples was treated with a solution of hydrochloric acid 25 ml/l (Sp. gr. 1.18) and chromic acid 10 g/l for 5 minutes at room temperature. The mandrel was then thoroughly washed with distilled water and electroforming was carried out from an acid copper sulphate bath for a predetermined time. The foil was then removed from the mandrel, washed thoroughly

and dried. The mandrel facing surface of the foil was found to be lustrous, smooth and free from pores and wrinkles.

Example 4

304 stainless steel sheets of size 600 mm x 600 mm x 3 mm were polished, buffed, degreased and electrocleaned as indicated above. The mandrel was then treated with hydrochloric acid (Sp.gr. 1.18) 50 ml/l and chromic acid 25 g/l for 2 minutes at room temperature. The mandrel was then washed thoroughly with distilled water and transferred to an acid copper sulphate bath and electroformed for a predetermined time. The foil was then removed from this mandrel, washed thoroughly and dried. The mandrel facing surface was found to be lustrous, smooth and free from pores and wrinkles.

Example 5

316 stainless steel sheets of size 300 mm x 300 mm x 3 mm were pre-cleaned as before. The sheet was then treated with sodium hydroxide 5 g/l and 20 g/l potassium ferricyanide for 10 minutes. The mandrel was then thoroughly washed with distilled water and transferred to an acid copper sulphate electroforming bath. Electroforming was carried out for a predetermined time. The foil was then removed from the mandrel, washed ~~through~~ thoroughly and dried. The mandrel facing side of the foil was found to be lustrous, smooth and free from wrinkles and pores.

Example 6

302 stainless steel mandrel of size 600 mm x 600 mm x 6 mm were precleaned as before. The mandrel was then treated with a solution containing sodium hydroxide 30 g/l and potassium ferricyanide 100 g/l for 2 minutes. The mandrel was washed thoroughly with distilled water. Electroforming was carried out for a predetermined time from an acid copper sulphate bath. The foil was then removed from the mandrel, washed and dried. The mandrel facing side of the foil was found to be lustrous, smooth, pores and wrinkles free.

We claim :

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1. Improved process for pretreatment of stainless steel mandrels used in electroforming of copper foils comprising polishing, buffing, degreasing and electrocleaning the mandrel surface and then treating the same with an aqueous acidic or alkaline oxidising solution containing as an oxidising agent cupric chloride, chromic acid or potassium ferricyanide at room temperature to obtain a mandrel with a shiny surface.

2. Process as claimed in claim 1 wherein the oxidising solution contains as an oxidising agent 10-25 g/l cupric chloride.

3. Process as claimed in claim 1 wherein the oxidising solution contains as an oxidising agent 10-50 g/l chromic acid.

4. Process as claimed in claim 1 wherein the oxidising solution contains as an oxidising agent 20-100 g/l potassium ferricyanide.

5. Process as claimed in claim 1 wherein the oxidising solution contains 250-300 ml/l of hydrochloric acid.

6. Process as claimed in claim 1 wherein the oxidising solution contains 5-30 g/l of sodium hydroxide.

7. Improved process for the pre-treatment of stainless steel mandrels used in electroforming of copper foils substantially as herein described and illustrated.

Dated this 11th day of December 1979.

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